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POLYDISPERSE DRY COMPOSITIONS FOR SLIP ENAMELING OF THIN-SHEET STEEL

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The particulars of obtaining polydisperse dry compositions for slip enameling of low-carbon steel are examined. The effect of the deflocculant xanthum gum on the technological and rheological properties of slips and the quality of enamel coatings are investigated.

Key words: polydisperse dry compositions, Ready to Use, viscosity, deflocculant, xanthum gum.

In recent years ready-to-use mixes have been used in many countries for slip enameling of thin-sheet steel. Some European companies producing enamel frits and powders for electrostatic deposition also manufacture so-called Premix, Ready-to-Use (RTU), and Ready-to-Mill powders [1].

Such composite mixes make it possible to eliminate the milling division as well as slip storage and loading facilities.

There are two known methods for making dry mixes for slip enameling [2]: dry milling of all components (frits, clayey components, refractory fillers, organic and inorganic stabilizers for suspensions) and wet milling of the same components followed by dry milling of the slip obtained.

One sphere of enameling where such mixes are widely used is the manufacture of electric water heaters (EWH) [3]. RTU mixes are supplied to these enterprises in Ukraine from abroad. Because these materials are in high demand now is the time to give high priority to the development domestic mixtures of this type and the technology for producing them.

The objective of the present work was to obtain from dry polydisperse compositions slips whose properties are similar to those of the slips made by conventional milling.

Because the production of dry mixes by the second method is energy-intensive the first method of production — dry milling of all components in the composition — was used to obtain such materials.

Chemically stable, no-primer, glass enamel based on the system R_2O–RO–Al_2O_3–ZrO_2–B_2O_3–SiO_2, where R_2O represents sodium and potassium oxides and RO calcium oxide, was used as the glass component for comminution. Quartz sand and $ZrSiO_4$ were used as the refractory fillers; Ch-0 Chasov-Yarskoe clay, bentonite, and aerosil were used to stabilize the suspension; and, sodium nitrate, borax, and magnesium carbonate were used as electrolytes. The compositions of the dry mixture studied were as follows (parts by weight): frit — 100; quartz sand — 5 – 15; zircon — 0 – 5; aerosil — 0 – 5; Ch-0 clay — 2 – 6; bentonite — 0.1 – 0.5; sodium nitrite $NaNO_2$ — 0.05 – 0.25; borax $Na_2B_4O_7 \cdot 10H_2O$ — 0.1 – 0.5; magnesium carbonate $MgCO_3$ — 0.05 – 0.5.

The mixtures were prepared in a laboratory ball mill by dry milling on a No. 015 sieve to residue 3% of the dry powder mass. The dry mixtures were carefully mixed with water (40 mass parts) to form a uniform suspension, which was kept standing for 12 h. A slip obtained by conventional methods from an initial composite mixture with the indicated composition with 40 mass parts water added was studied at the same time. The viscosity of the slips obtained was determined on a Brookfield rotational viscometer by the procedure of [4].

It is well know that in conventional wet milling water plays the determining role in obtaining slip. Water has a complex effect on the colloidal-chemical processes occurring in the system disperse phase — dispersion medium. Processes such as adsorption, ion exchange, and electric double layer (EDL) formation occur. These processes determine the interaction of the liquid and solid phases and form the corresponding qualitative characteristics of the slip. The slip properties are determined by the deflocculation of the solid phase, expressed as a loss of the capability to form clumps of

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adhering particles or floccules, which results in the appearance of conglomerates. In this case the particles of enamel frit and other solid components are in a deflocculated state (separated from one another by liquid), and the slip becomes stable and acquires required technological properties. After grinding, the slip is allowed to age for 24 – 48 h, mainly to stabilize its properties. Processes destroying the surface of the enamel grains and subsequent colloidal break-up and swelling of the clay and bentonite accompanied by the adsorption of ions on the surface of the particles continue [5]. These processes, which intensive during the first few days after milling, all slow down with time.

A distinguishing feature of the technology for obtaining slips from RTU mixtures is that the slip structure forms in only 6 – 12 h prior to deposition on the workpiece. In this case adsorption, ion exchange, and EDL formation occur only within this time frame. For this reason, to accelerate slip preparation and improve the technological properties of the slip substances promoting deflocculation of the particles — surfactants and high-molecular substances — are added to RTU mixtures [2, 5].

The most important rheological characteristic of enamel slips is viscosity. Enamel slips are so-called structured systems, for which non-Newtonian, or structural, viscosity is characteristic.

According to [5], enamel slips with satisfactory rheological properties must have structural viscosity $\eta = 0.1 - 0.2$ Pa · sec when deposited on a workpiece with a complicated shape. Here the critical velocity v_{cr} — the maximum velocity at which structural-circulatory motion appears — must be taken into consideration, while the structural viscosity reaches $\eta = 1.5$ Pa · sec.

In the present work the viscosity of slips made from the compositions having the components presented and obtained by the conventional wet method (Sh-1) and dry milling (Sh-2, -3) is studied. The Sh-3 slip differed from Sh-2 by the addition of a high-molecular compound (HMC) — xanthum gun, used as a deflocculant.

As plots of the function $\eta = f(\gamma)$ show, for all the experimental suspensions a transition to practically constant viscosity at high strain rates $\gamma = 4$ sec^{-1} is characteristic when definite values of γ are reached. For small values of γ of the experimental suspensions the viscosity depends strongly on the method used to obtain the suspensions. This is observed on the plots of the function $\eta = f(\gamma)$ when the viscosity assumes constant values with increasing strain rate (Fig. 1 – 3). The viscosity curves of all slips obtained have a similar character for high strain rates and different considerably at low rates. For example, the viscosity of the slip Sh-2 (Fig. 1) is high $\eta = 28$ Pa · sec for high initial strain rates and low values $\eta = 1.6$ Pa · sec at which structural-circulatory motion appears, while xanthum gum addition greatly decreases this index to $\eta = 14$ Pa · sec for the initial shear rates in slip Sh-3 (Fig. 2) and increases it $\eta = 2.8$ Pa · sec for structural-circulatory motion. It should be underscored that this is practically twice the value of the index in the slip Sh-1 (milled with water) $\eta = 6.8$ Pa · sec (Fig. 3). When the slip Sh-1 reaches structural-circulatory $\eta = 3.4$ Pa · sec approaches the value for slip Sh-3. This is probably due to the completion of ion exchange, adsorption, and formation of a double layer in the slip Sh-1 obtained by the conventional method. For slips made from dry mixtures these processes appear only after mixing with water, while for conventional slips they already

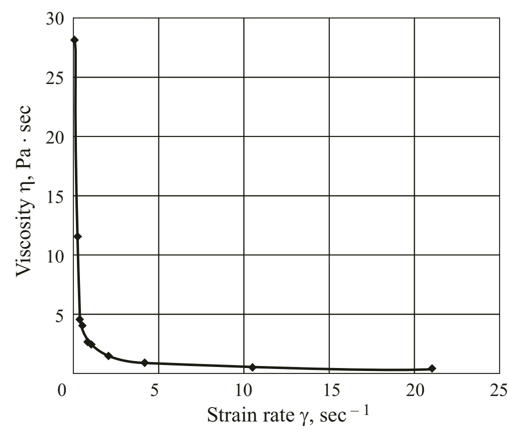

Fig. 1. $\eta = f(\gamma)$ for slip Sh-2.

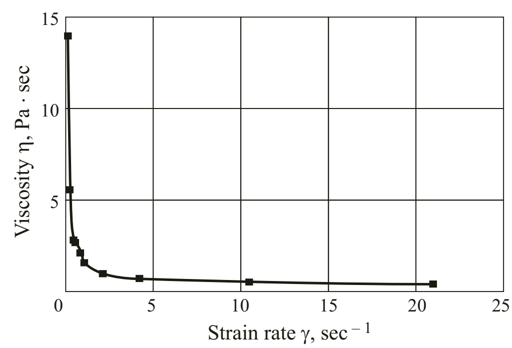

Fig. 2. $\eta = f(\gamma)$ for slip Sh-3.

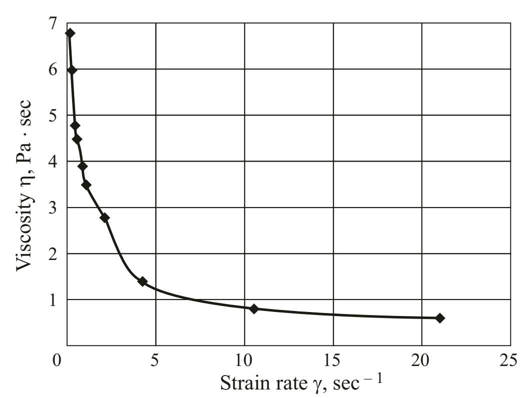

Fig. 3. $\eta = f(\gamma)$ for slip Sh-1.

appear during milling. As one can see from the plots of the function $\eta = f(\gamma)$, when the structural-circulatory motion is reached the viscosity of the conventional slip is very close to that of the slip made from a dry mix with a HMC. It is this index that characterizes the satisfactory coverage properties of slip deposited on steel workpieces.

The sedimentation stability of slip made from a dry mix without HMC was 85% — the working index of this property must be in the range 96 – 98%. The stability of slip made from mix with HMC and the stability of slip milled by the conventional methods were within these limits.

The slips obtained were deposited on a sample of 1.5 mm thick 08kp low-carbon steel. The slip Sh-2 made from a dry mix without xanthum gum did not deposit well, flowing off without being held back by the substrate, because of the low coverage 4.2 g/dm^2. It should be noted that in the case of steel internal tanks in water heaters this index must be at least 8 g/dm^2. The coverage for the slips Sh-1 and Sh-3 was 8.5 and 9.0 g/dm^2, respectively. The samples with the deposited layer were dried at temperature 200 °C and kilned at temperature 840°C for 4 min. The coating made from the Sh-2 slip based on a dry mix with no deflocculating additive was characterized by variable thickness, while the coatings made of the slip Sh-3 (dry mix with xanthum gum addition) and slip Sh-1 (obtained by wet milling) were characterized by uniform thickness and absence of defects.

CONCLUSIONS

It was established that the method used to obtain slips from polydisperse dry compositions affects their rheological properties and the quality of the coating obtained. The dependence of the function $\eta = f(\gamma)$ for slips obtained from RTU mixtures on the presence of a deflocculant was determined. The properties of the enamel slips obtained from the mixtures developed are similar to those of conventional slips, and the unconventional slips can be used in the manufacture of electric water heaters.

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